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Bridging Binding Modes of Phosphine-Stabilized Nitrous Oxide to $Zn(C_6F_5)_2$**

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General Considerations. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing standard Schlenk-line and glovebox techniques. Solvents (pentane, hexanes, CH_2Cl_2) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored under N_2. Cyclohexane was distilled under N_2 from Na/benzophenone while bromobenzene was distilled under N_2 from CaH_2. CD_2Cl_2 was vacuum transferred from CaH_2, degassed and stored under N_2. $^tBu_3P$ (Strem Chemicals), N_2O (Sigma-Aldrich; 99%) and $^{15}N_2O$ (Cambridge Isotope Laboratories; 99.9%, 98.8% ^{15}N enriched) were used as received. $Zn(C_6F_5)_2$ (Sigma-Aldrich; 97%) was recrystallized from toluene at -35 °C, yielding the toluene adduct, tol·$Zn(C_6F_5)_2$. The reagent $B(C_6H_4F)_3$[1] was prepared according to literature procedures. ^1H, ^{11}B, ^{13}C, ^{15}N, ^{19}F and ^{31}P NMR spectra were recorded at 25 °C, unless otherwise stated, on a Varian NMR System 400 MHz or Bruker Avance III 400 MHz spectrometer and were referenced using (residual) solvent resonances relative to $SiMe_4$ (^1H, ^{13}C), or relative to an external standard (^{11}B: $(Et_2O)BF_3$, ^{19}F: $CFCl_3$, ^{31}P: 85% H_3PO_4, ^{15}N: $NH_3(l)$ via the ^{15}N resonance of 90% formamide in DMSO-d_6 at 112 ppm).[2] Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer.

$^tBu_3PN_2OB(C_6H_4F)_3$ (1). A 50 mL schlenk tube was charged with $B(C_6H_4F)_3$ (0.212 g, 0.716 mmol) and $^tBu_3P$ (0.145 g, 0.717 mmol) in bromobenzene (10 mL). The pale yellow solution was subjected to 3 freeze-pump-thaw cycles using liquid nitrogen to degas the solution. The solution was left stirring under an atmosphere of N_2O for 12 hours at room temperature. At this time, the solution was cloudy and pale yellow. Pentane (10 mL) was added precipitating a white solid. The solid was isolated by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.312 g (80 %). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.33 (m, 6H, *o*-C_6H_4F), 6.87 (m, 6H, *m*-C_6H_4F), 1.38 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, 25 °C): δ 6.69 (s). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C) partial: δ 161.25 (br d, $^1J_{C\text{-}F}$ = 247 Hz, *p*-C_6H_4F), 135.54 (br s, *m*-C_6H_4F), 113.50 (br s, *o*-C_6H_4F), 41.31 (d, $^1J_{C\text{-}P}$ = 31 Hz, P{*C*$(CH_3)_3$}), 29.85 (s, P{C(*C*$H_3)_3$}. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -120.87 (s). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 65.38 (s). Anal. Calcd. for $C_{30}H_{39}BF_3N_2OP$: C, 66.43; H, 7.25; N, 5.16. Found: C, 66.25; H, 7.27; N, 5.17 %.

$^tBu_3P^{15}N_2OB(C_6H_4F)_3$ (1-^{15}N). A J. Young NMR tube containing a solution of $B(C_6H_4F)_3$ (0.025 g, 0.084 mmol) and $^tBu_3P$ (0.017 g, 0.084 mmol) in C_6H_5Br (0.5 mL) was subjected to 3 freeze-pump-thaw cycles using liquid nitrogen to degas the solution and backfilled with $^{15}N_2O$. After standing overnight, the product was precipitated by addition of hexanes (5 mL). The product was allowed to settle and the solvent was decanted followed by washing with hexanes (2 x 1 mL). The solid was dried *in vacuo* for 1 hour. ^1H and ^{19}F NMR spectra were identical to **1**. ^{15}N NMR (40.6

MHz, CD_2Cl_2, 25 °C): δ 588.75 (dd, $^2J_{N\text{-}P}$ = 19 Hz, $^1J_{N\text{-}N}$ = 18 Hz, PN*N*O), 367.61 (dd, $^1J_{N\text{-}P}$ = 61 Hz, $^1J_{N\text{-}N}$ = 18 Hz, P*N*NO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 64.27 (dd, $^1J_{P\text{-}N}$ = 61 Hz, $^2J_{P\text{-}N}$ = 19 Hz).

[^{t}Bu$_3$PN$_2$OZn(C$_6$F$_5$)$_2$]$_2$ (2). A 20 mL scintillation vial was charged with **1** (0.100 g, 0.184 mmol) and tol·Zn(C$_6$F$_5$)$_2$ (0.091 g, 0.185 mmol) in CH_2Cl_2 (5 mL). The solution was initially opaque but cleared after a few seconds of stirring. The reaction was left stirring for 1 hour at room temperature. At this time, the solution was cloudy. Hexanes (10 mL) was added precipitating a fine white solid. The solid was isolated by filtration, washed with hexanes (3 x 5 mL) and dried *in vacuo* for 2 hours. Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at -35 °C. Yield: 0.118 g (99 %). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.51 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 149.30 (br d, $^1J_{C\text{-}F}$ = 228 Hz, *o*-C$_6$F$_5$), 140.46 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *p*-C$_6$F$_5$), 136.90 (br d, $^1J_{C\text{-}F}$ = 259 Hz, *m*-C$_6$F$_5$), 120.71 (s, *ipso*-C$_6$F$_5$), 41.65 (d, $^1J_{C\text{-}P}$ = 31.65, P{*C*(CH$_3$)$_3$}), 29.70 (s, P{C(*C*H$_3$)$_3$}). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -117.44 (m, *o*-C$_6$F$_5$), -157.71 (t, $^3J_{F\text{-}F}$ = 19 Hz, *p*-C$_6$F$_5$), -162.64 (m, *m*-C$_6$F$_5$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 66.50 (s). Anal. Calcd. for $C_{48}H_{54}F_{20}N_4O_2P_2Zn_2$: C, 44.63; H, 4.21; N, 4.34. Found: C, 44.32; H, 4.14; N, 4.66 %.

[^{t}Bu$_3$P^{15}N$_2$OZn(C$_6$F$_5$)$_2$]$_2$ (2-^{15}N). A 10 mL scintillation vial was charged with **1-^{15}N** (0.023 g, 0.042 mmol) and tol·Zn(C$_6$F$_5$)$_2$ (0.021 g, 0.043 mmol) in CH_2Cl_2 (3 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, hexanes (5 mL) was added precipitating a fine white solid. The solid was allowed to settle and the solvent was decanted followed by washing of the solid with hexanes (2 x 1 mL). The product was dried *in vacuo* for 1 hour. ^1H and ^{19}F NMR spectra are identical to **2**. ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 599.07 (dd, $^2J_{N\text{-}P}$ = 9.3 Hz, $^1J_{N\text{-}N}$ = 18 Hz, PN*N*O), 317.97 (dd, $^1J_{N\text{-}P}$ = 54 Hz, $^1J_{N\text{-}N}$= 18 Hz, P*N*NO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 65.83 (dd, $^1J_{P\text{-}N}$ = 54 Hz, $^2J_{P\text{-}N}$ = 9.3 Hz).

(^{t}Bu$_3$N$_2$OZn(C$_6$F$_5$)$_2$)$_2$Zn(C$_6$F$_5$)$_2$ (3). Method I. A 20 mL scintillation vial was charged with **1** (0.060 g, 0.111 mmol) and tol·Zn(C$_6$F$_5$)$_2$ (0.082 g, 0.167 mmol) in CH_2Cl_2 (10 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing of the solid with pentane (3 x 5 mL). The product was dried *in vacuo* for 1 hour. Yield: 0.076 g (81 %). **Method II.** A 20 mL scintillation vial was charged with **2** (0.037 g, 0.029 mmol) and tol·Zn(C$_6$F$_5$)$_2$ (0.014 g, 0.028 mmol) in CH_2Cl_2 (10 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing of the solid with pentane (3 x 5 mL). The product was dried *in vacuo* for 1 hour. Yield:

0.037 g (77 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at -35 °C. ^{1}H NMR (400MHz, CD_2Cl_2, 25 °C): δ 1.46 (d, 27H, $^{3}J_{H\text{-}P}$ = 14 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 149.26 (br d, $^{1}J_{C\text{-}F}$ = 245 Hz, *o*-C_6F_5), 140.17 (br d, $^{1}J_{C\text{-}F}$ = 224 Hz, *p*-C_6F_5), 136.41 (br d, $^{1}J_{C\text{-}F}$ = 241 Hz, *m*-C_6F_5), 118.95 (s, *ipso*-C_6F_5), 41.86 (d, $^{1}J_{C\text{-}P}$ = 30 Hz, P{*C*$(CH_3)_3$}), 29.59 (s, P{C(*C*$H_3)_3$}). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -117.56 (m, *o*-C_6F_5), -156.73 (t, $^{3}J_{F\text{-}F}$ = 19 Hz, *p*-C_6F_5), -162.42 (m, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 68.54 (s). Anal. Calcd. for $C_{60}H_{54}F_{30}N_4O_2P_2Zn_3{\cdot}CH_2Cl_2$: C, 41.25; H, 3.18; N, 3.15. Found: C, 41.73; H, 3.39; N, 3.49 %.

(^{t}Bu$_3$PN$_2$OZn(C$_6$F$_5$)$_2$)$_2$Zn(C$_6$F$_5$)$_2$ at -75 °C . A J. Young NMR tube was charged with **3** (0.006 g, 0.004 mmol) in CD_2Cl_2 (0.5 mL). The ^{19}F NMR spectrum was recorded at -75 ºC. ^{19}F NMR (376 MHz, CD_2Cl_2, -75 °C): δ -117.43 (br s, *o*-C_6F_5), -117.93 (br s, *o*-C_6F_5), -156.26 (t, $^{3}J_{F\text{-}F}$ = 19 Hz, *p*-C_6F_5), -157.65 (t, $^{3}J_{F\text{-}F}$ = 18 Hz, *p*-C_6F_5), -161.81 (br s, *m*-C_6F_5), -162.30 (br s, *m*-C_6F_5).

(^{t}Bu$_3$N$_2$OZn(C$_6$F$_5$)$_2$)$_2$Zn(C$_6$F$_5$)$_2$ (3-^{15}N). A 10 mL scintillation vial was charged with **1-^{15}N** (0.010 g, 0.018 mmol) and tol·Zn$(C_6F_5)_2$ (0.014 g, 0.028 mmol) in CH_2Cl_2 (3 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, hexanes (5 mL) was added precipitating a fine white solid. The solid was allowed to settle and the solvent was decanted followed by washing with hexanes (2 x 1 mL). The soild was then dried *in vacuo* for 1 hour. ^{1}H and ^{19}F NMR spectra are identical to **3**. ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 595.17 (dd, $^{2}J_{N\text{-}P}$ = 9.4 Hz, $^{1}J_{N\text{-}N}$ = 18 Hz, PN*N*O), 323.78(dd, $^{1}J_{N\text{-}P}$ = 54 Hz, $^{1}J_{N\text{-}N}$ = 18 Hz, P*N*NO). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 68.22 (dd, $^{1}J_{P\text{-}N}$ = 54 Hz, $^{2}J_{P\text{-}N}$ = 9.4 Hz).

^{t}Bu$_3$PN$_2$O(Zn(C$_6$F$_5$)$_2$)$_2$ (4). Method I. A 20 mL scintillation vial was charged with **1** (0.064 g, 0.118 mmol) and tol·Zn$(C_6F_5)_2$ (0.116 g, 0.236 mmol) in CH_2Cl_2 (10 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing with pentane (3 x 5 mL). The solid was dried *in vacuo* for 1 hour. Yield: 0.099 g, (80 %). **Method II.** A 20 mL scintillation vial was charged with **2** (0.060 g, 0.046 mmol) and tol·Zn$(C_6F_5)_2$ (0.046 g, 0.094 mmol) in CH_2Cl_2 (8 mL). The cloudy, faintly yellow solution was left stirring for 1 hour at room temperature. At this time, hexanes (10 mL) was added precipitating a fine white powder. The solid was allowed to settle and the solvent was decanted followed by washing with hexanes (3 x 5 mL). The solid was dried *in vacuo* for 1 hour. Yield: 0.068 g (70 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/cyclohexane solution at 25 °C. ^{1}H NMR (400MHz, CD_2Cl_2, 25 °C): δ 1.43 (d, 27H, $^{3}J_{H\text{-}P}$ = 14 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 149.41 (br d, $^{1}J_{C\text{-}F}$ = 224 Hz, *o*-C_6F_5), 140.97 (br d, $^{1}J_{C\text{-}F}$ = 248 Hz, *p*-C_6F_5), 137.00 (br d, 262 Hz, *m*-C_6F_5), 118.29 (s, *ipso*-C_6F_5), 42.04 (d, $^{1}J_{C\text{-}P}$ = 30 Hz, P{*C*$(CH_3)_3$}), 29.53 (s,

P{C(*C*H$_3$)$_3$}). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -117.62 (m, *o*-C_6F_5), -156.26 (t, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -162.18 (m, *m*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 71.65 (s). Anal. Calcd. for $C_{36}H_{27}F_{20}N_2OPZn_2 \cdot 0.5CH_2Cl_2$: C, 40.30; H, 2.59; N, 2.57. Found: C, 40.05; H, 2.80; N, 2.78 %.

^{t}Bu$_3$PN$_2$O(Zn(C$_6$F$_5$)$_2$)$_2$ at -75 °C . A J. Young NMR tube was charged with **4** (0.006 g, 0.006 mmol) in CD_2Cl_2 (0.5 mL). The ^{19}F NMR spectrum was recorded at -75 ºC. ^{19}F NMR (376 MHz, CD_2Cl_2, -75 °C): δ -117.61 (d, $^3J_{F\text{-}F}$ = 20 Hz, *o*-C_6F_5), -118.15 (d, $^3J_{F\text{-}F}$ = 20 Hz, *o*-C_6F_5), -154.85 (t, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -155.36 (t, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -161.10 (t, $^3J_{F\text{-}F}$ = 19 Hz, 2 x *m*-C_6F_5).

^{t}Bu$_3$P^{15}N$_2$O(Zn(C$_6$F$_5$)$_2$)$_2$ (4-^{15}N). A 10 mL scintillation vial was charged with **2-^{15}N** (0.014 g, 0.011 mmol) and $(C_6F_5)_2Zn$·toluene (0.010 g, 0.020 mmol) in dichloromethane (3 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, hexanes (5 mL) was added precipitating a fine white solid. The solid was allowed to settle and the solvent was decanted followed by washing with hexanes (2 x 1 mL). The product was dried *in vacuo* for 1 hour. ^{1}H and ^{19}F NMR spectra are identical to **4**. ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 582.52 (dd, $^2J_{N\text{-}P}$ = 11 Hz, $^1J_{N\text{-}N}$ = 17 Hz, PN*N*O), 349.33 (dd, $^1J_{N\text{-}P}$ = 54 Hz, $^1J_{N\text{-}N}$ = 17 Hz, P*N*NO). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 71.99 (dd, $^1J_{P\text{-}N}$ = 54 Hz, $^2J_{P\text{-}N}$ = 11 Hz).

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